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Modified Magnesium Hydride and Calcium Borohydride for High-Capacity Thermal Energy Storage (PREPRINT)

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14. ABSTRACT

MgH_2, and $Ca(BH_4)_2$ are potential thermal energy storage (TES) materials that possess extraordinarily high inherent thermal energy densities of up to 2 MJ/kg. However, the high desorption temperatures at atmospheric pressure [>300°C for $Ca(BH_4)_2$, >400°C for MgH_2] coupled with slow kinetics represent significant challenges for their use in TES. In order to address these challenges, the present work focuses on the development of new modification approaches based on nanostructuring via high-energy vibratory ball milling and catalytic enhancement using pure Ni and Ni alloys. Our work reveals that high-energy vibrating-mill technique with ball-to-powder weight ratio as low as 13:1 can produce MgH_2 powders with nanocrystallites after 2h of milling. MgH_2 milled with Ni (5 wt%) and Ni_5Zr_2(5 wt%) catalysts for 2 h showed apparent activation energies, E_A of 81 and 79 kJ/mo1, respectively, corresponding to ~50% decrease in E_A and~100%°C decrease in the decomposition temperature (T_{dec}). On the other hand, the decomposition reaction of $Ca(BH_4)_2$ does not seem to be catalyzed by the Ni-based catalysts tested.

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MODIFIED MAGNESIUM HYDRIDE AND CALCIUM BOROHYDRIDE FOR HIGH-CAPACITY THERMAL ENERGY STORAGE

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ABSTRACT

MgH_2 and $Ca(BH_4)_2$ are potential thermal energy storage (TES) materials that possess extraordinarily high inherent thermal energy densities of up to 2 MJ/kg. However, the high desorption temperatures at atmospheric pressure [>300°C for $Ca(BH_4)_2$, >400°C for MgH_2] coupled with slow kinetics represent significant challenges for their use in TES. In order to address these challenges, the present work focuses on the development of new modification approaches based on nanostructuring via high-energy vibratory ball milling and catalytic enhancement using pure Ni and Ni alloys. Our work reveals that high-energy vibrating-mill technique with ball-to-powder weight ratio as low as 13:1can produce MgH_2 powders with nanocrystallites after 2h of milling. MgH_2 milled with Ni (5 wt%) and Ni_5Zr_2 (5 wt%) catalysts for 2 h showed apparent activation energies, E_A of 81 and 79 kJ/mol, respectively, corresponding to ~50% decrease in E_A and ~100°C decrease in the decomposition temperature (T_{dec}). On the other hand, the decomposition reaction of $Ca(BH_4)_2$ does not seem to be catalyzed by the Ni-based catalysts tested.

INTRODUCTION

The development of novel and efficient thermal energy storage (TES) materials remains a major challenge in addressing needs in a variety of areas from intermittent solar energy harvesting to thermal management of transient, high-flux heat loads. A variety of passive materials have been developed and employed for TES including paraffin waxes, water tanks, and low-capacity reversible metal hydrides, among others. Paraffin wax has been used as a TES medium for decades [1,2,3,4]. However, the current state-of-art packaging technology for paraffin wax reduces the system level heat storage capacity by 75%, i.e. from 250 kJ/kg down to 65 kJ/kg. Other material systems of possible interest are summarized in Table 1; notably, paraffins and liquid metals have impractically low inherent enthalpies of phase change when normalized by mass. In fact, the only two example materials that exceed 1 MJ/kg are water (liquid-vapor) and metal hydride (MgH_2). Regarding water, the slow kinetics of boiling/evaporation, limited largely by the nucleation, ebullition, and departure time

of ~10 ms for each bubble [5], and the prospective need to handle large quantities of vapor make it less practical.

TABLE 1 – INHERENT MATERIAL ENTHALPY OF PHASE CHANGE AND/OR REACTION FOR CANDIDATE THERMAL STORAGE MATERIALS

Material	ΔH (MJ/kg)
Metal Hydride: MgH_2 (solid-vapor, w/ reaction)	2.83
Water (liquid-vapor)	2.25
Water (solid-liquid)	0.33
Metal Hydride: $LaNi_5H_6$ (solid-vapor, w/ reaction)	0.23
Paraffin waxes (solid-liquid)	0.20-0.25
Indium (solid-liquid)	0.03

Metal hydrides offer a potential materials solution, enabled by the uniquely high formation enthalpy of hydrogen gas, but they also offer significant challenges to be overcome. First, we note that not all metal hydrides have high energy storage capacities (cf., $LaNi_5H_6$ as shown in Table 1). In fact, some well-known intermetallic metal hydrides have been studied recently for reversible and reasonably fast thermal storage [6]. However, the low thermal energy density of such 'classical' hydrides renders them poorly suited for the transformative approaches envisioned in thermal management. However, some metal hydrides do approach the target storage density. Magnesium hydride (MgH_2) is a well-studied example [7], but the high temperatures required for hydrogen release and very slow kinetics make it impractical for the present application. Fortunately, the broader metal hydride research community has been very active recently in developing new hydrides for fuel cell vehicles, but in that application low reaction enthalpies are desired because high reaction enthalpies decrease overall efficiency and create severe cooling problems upon hydrogenation (i.e., fueling).

Because of the emphasis on hydrogen storage for fuel cell vehicles, metal hydrides with high heats of reaction have been virtually ignored in recent research compared to those with moderate-to-low reaction heats. Conversely, our work focuses on metal hydrides that offer extraordinarily high inherent thermal storage capacity, while also providing innovative new routes for controllable kinetics enhancement and high effective thermal conductivity. Yet to access this large thermal density under rapid heating conditions required for several important applications, efficient heat flow, reduced desorption temperatures, and fast chemical kinetics are required, and therefore, innovative material enhancement solutions must be developed, including the introduction of thermal additives, doping of metal hydrides with catalysts, and nanostructuring of metal hydride powders.

Further, we note that the use of hydrogen gas produced from a metal hydride is not useful merely because of its tremendously high enthalpy (which derives from correspondingly high entropy). Hydrogen gas as a thermal transport medium is simply unparalleled. For example, the electrical power generation industry uses hydrogen extensively (often produced by on-site electrolysis) to provide high-rate cooling of turbine generator windings [8]. The use of hydrogen for such massive-scale cooling is not surprising, given the comparative summary of its thermal properties shown in Table 2. The summary indicates that the common thermophysical properties of hydrogen are an order of magnitude superior to those of other common reactive gases. Only He gas, which is inert, even approaches the thermal performance of hydrogen. Furthermore, hydrogen's high specific gas constant makes it uniquely suitable for ultra-fast expansion cooling.

TABLE 2 – THERMOPHYSICAL PROPERTIES OF COMMON REACTIVE GASES AT ROOM TEMPERATURE AND PRESSURE

Gas	Specific Heat, C_p (kJ/kgK)	Thermal Conductivity κ (W/mK)	Specific Gas Constant *R* (kJ/kgK)
Hydrogen, H_2	14.21	0.180	4.12
Air	1.00	0.026	0.287
Ammonia, NH_3	2.13	0.024	0.488
Carbon dioxide, CO_2	0.84	0.016	0.189
Steam, H_2O	1.87	0.020 (at BP)	0.461

In this study, the effects of high-energy vibratory ball milling and catalyst doping (Ni and Ni alloys) on the dehydrogenation reaction of MgH_2 and $Ca(BH_4)_2$ are studied using simultaneous differential scanning calorimetry and thermogravimetry (DSC/TGA). Ni is chosen as the catalyst because of its ability to break hydrogen bonds during hydrogenation and enhance recombination of hydrogen atoms during dehydrogenation, and Ni catalyzed MgH_2 reactions have shown better kinetics and lower decomposition temperatures than other transition metals [9,10,11].

EXPERIMENTAL PROCEDURE

MgH_2, $Ca(BH_4)_2$, $LaNi_5$, and Ni_5Zr_2 powders were purchased from Sigma-Aldrich while Ni metal nanopowder (< 100 nm in size and 99.9% in purity) was purchased from American Elements. The as-received hydrides and catalyst - hydride mixtures (2 and 5 wt% of catalysts) were ball milled in a SPEX SamplePrep 8000M Mixer/Mill [high-energy shaker

(vibratory) mill] which combines strong shearing and impact forces to mix, blend, and reduce particle size. The hydrides were milled in a 65 cm^3 stainless steel vial using 10 steel grinding balls (7 mm in diameter) under Ar environment. The ball-to-powder weight ratio was 13:1, which is consistent with the recommended range of 10 – 100 [11]. Samples were handled in an Ar glove box with the amount of oxygen and water vapor present being less than 0.1 ppm each, to prevent oxidation and/or hydroxide formation.

Differential Scanning Calorimetry (DSC) and thermogravimetry (TGA) were performed using an SDT 2960 Simultaneous DSC-TGA instrument (TA Instruments). All measurements were carried out with 5 – 10 mg of sample; the temperature was linearly increased to 500°C using a ramp rate of 5°C/min in a stream of Ar (~50 sccm) to prevent oxidation. The apparent activation energy, E_A, of the dehydrogenation reactions was determined using the Kissinger method. The Kissinger equation [12] given in equation 1 involves an analysis of the sensitivity of the maximum of the desorption DSC peak (T_{max}) to the applied heating rate (β) [11].

$$\frac{d\ln\left(\frac{\beta}{T_{max}^2}\right)}{d\left(\frac{1}{T_{max}}\right)} = -\frac{E_A}{R} \qquad (1)$$

R represents the gas constant. E_A is determined from a linear plot of $\ln\frac{\beta}{T^2}$ versus $\frac{1000}{T}$. The heating rates used for this analysis were 5, 10 and 20°C/min.

The morphological characterization of the hydride samples was conducted using a field emission scanning electron microscope (Hitachi S5200). Samples were prepared by immobilizing 3 – 5 mg of powder on a sticky Cu tape and images were taken under secondary electron mode.

RESULTS AND DISCUSSION

The effect of high-energy milling for different durations on the decomposition temperature (T_{dec}) of MgH_2 was studied in order to optimize the milling conditions. As shown in Figure 1, the DSC profiles are characterized by a single endothermic peak, which corresponds to the decomposition of the hydride. The T_{dec} of the as-received MgH_2 sample occurs at 414°C while the T_{dec} for samples milled for 1, 2, 5, and 10 h are 374, 352, 363, and 371°C, respectively. It is believed that the small endothermic peak at 450°C is experimental artifact only. The reduction of T_{dec} by ~62°C while maintaining about the same peak area imply that the optimum milling time under these conditions is 2 h. Other workers have reported that a reduction in T_{dec} by up to 60°C typically requires prolonged milling. For instance, Varin et al. [13] reported a reduction in T_{dec} in the range of 40 – 60°C for the as-received MgH_2 after milling for 10 – 100 h. Therefore, a 60°C reduction in T_{dec} after 2 h milling is quite significant. The decrease in T_{dec} after milling has been attributed to the formation of nanograins, introduction of lattice strains, and phase transformation of tetragonal β-MgH_2 to orthorhombic γ-MgH_2 [11]. The effect of milling on the morphology and microstructure of the as-received MgH_2 is shown by the FESEM images in Figure 2. The as-received MgH_2 has a grain size of ~10 μm and the formation of fine grains is observed with increasing milling time. No Fe contamination was observed during XPS analysis of the milled samples suggesting that the reduction in T_{dec} observed is completely due to the milling of the hydride, not from the leaching of Fe from the stainless steel vial.

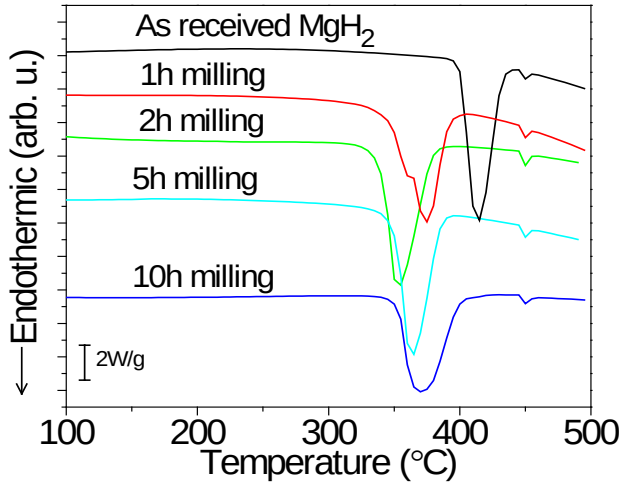

FIGURE 1 – DSC PROFILES OF MgH_2 SAMPLES MILLED FOR VARIOUS DURATIONS

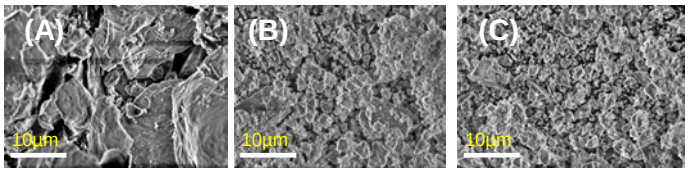

FIGURE 2 – FESEM IMAGES OF (A) AS-RECEIVED MgH_2 SHOWING THE MORPHOLOGIC CHANGE AFTER MILLING FOR (B) 2 h and (C) 5 h

Further, we examined the dehydrogenation reaction of MgH_2 milled with 2 and 5 wt% of Ni-based catalysts for 2h. Figure 3 shows the DSC results and corresponding TGA profiles of the as-received MgH_2, milled MgH_2, and MgH_2 doped with 2 wt% Ni_5Zr_2, $LaNi_5$, and Ni catalysts. The onset temperature (T_{onset}) and T_{dec} for the various samples are summarized in Table 3. The DSC results show a reduction in T_{dec} due to the catalytic effect of Ni and the Ni alloys, compared to the T_{dec} of MgH_2 milled for 2 h without catalyst. These results are consistent with a similar shift in decomposition temperature observed in the TGA profile. The catalytic effect of Ni appears to be marginally higher than for Ni_5Zr_2 or $LaNi_5$

because T_{dec} for the former is 324°C while the latter are 331 and 333°C, respectively. Also, the DSC results for MgH_2 milled with Ni_5Zr_2 and $LaNi_5$ have a shoulder at 350°C, which corresponds to the T_{dec} of MgH_2 milled in the absence of a catalyst. This suggests that unlike pure Ni, the Ni alloys do not seem to catalyze the dehydrogenation reaction completely. Hanada et al. [14] showed that the hydrogen desorption properties of Nb_2O_5-catalyzed MgH_2 are improved with increasing milling time in contrast to that of Ni-catalyzed MgH_2. Similarly, it is possible that the shoulder observed at 350°C may disappear with longer milling time.

TABLE 3 – PROPERTIES OF MgH_2 SAMPLES

Samples	Catalyst amount (wt%)	Milling time (h)	T_{onset} (°C)	T_{dec} (°C)
MgH_2 (Aldrich)	-	-	402	414
MgH_2	-	1	355	374
MgH_2	-	2	341	353
MgH_2	-	5	351	363
MgH_2	-	10	353	371
MgH_2/Ni_5Zr_2	2	2	306	331
$MgH_2/LaNi_5$	2	2	311	333
MgH_2/Ni	2	2	306	324
MgH_2/Ni_5Zr_2	5	2	293	318
$MgH_2/LaNi_5$	5	2	289	317
MgH_2/Ni	5	2	304	323

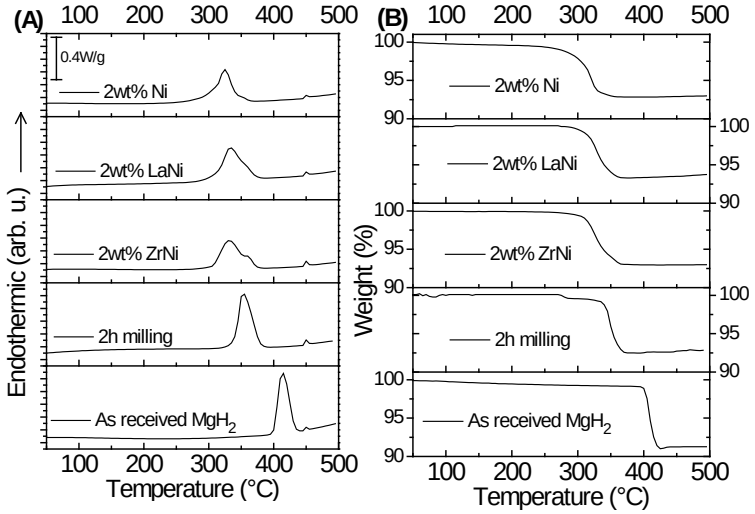

FIGURE 3 – DSC (A) AND CORRESPONDING TGA (B) PROFILES FOR THE AS-RECEIVED MgH_2, MILLED MgH_2, AND MgH_2 MILLED WITH 2 wt% CATALYSTS

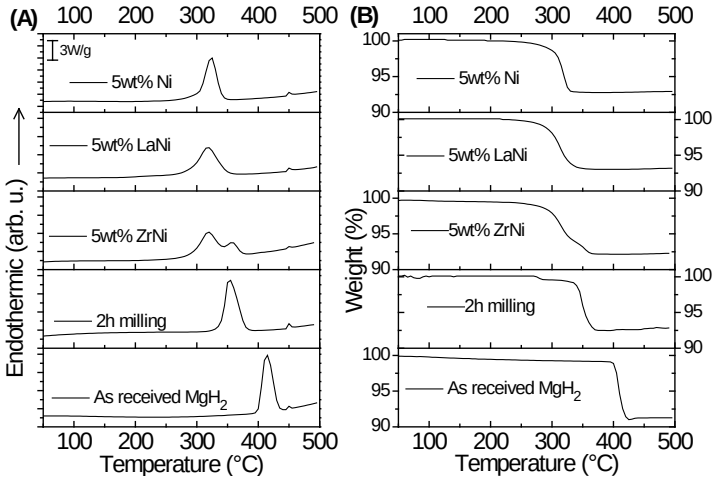

FIGURE 4 - DSC (A) AND CORRESPONDING TGA (B) PROFILES FOR THE AS-RECEIVED MgH_2, MILLED MgH_2, AND MgH_2 MILLED WITH 5 wt% CATALYSTS

The influence on milling MgH_2 with higher amounts of Ni-based catalysts (5 wt%) was also studied. Figure 4 shows the DSC profiles and corresponding TGA profiles of the as-received MgH_2, milled MgH_2, and MgH_2 doped with 5 wt% Ni_5Zr_2, $LaNi_5$, and Ni catalysts. The DSC profile of MgH_2 samples milled with Ni_5Zr_2 shows a double desorption peak at 319 and 350°C and the corresponding TGA profile also shows two distinct regions of weight loss at similar temperatures. This further suggests that Ni_5Zr_2 does not catalyze the entire reaction under the milling conditions used. In future experiments, longer milling time will be explored. As shown in Figure 4, the maximum of the endothermic peak is further reduced by ~10°C upon increasing the catalyst amount from 2 to 5 wt%. High-energy milling of the as-received MgH_2 with 5 wt% Ni or Ni_5Zr_2 has therefore resulted in ~100°C decrease in T_{dec}. The literature is replete with studies on the catalytic enhancement of hydrides [11], however most studies involve several hour of ball milling. For example, Yonkeu et al. [15] showed that using 2 mol% of body centered cubic-alloy $TiV_{1.1}Mn_{0.9}$ (BCC) decreases the T_{dec} of MgH_2 from 429.2°C to 368.3°C only after 80 h of ball milling. Although the current T_{dec} achieved at this stage of our work is still higher than the desired range for TES, the substantial decrease in T_{dec} achieved after only 2 h of milling is noteworthy. Our results suggest that further optimization of the high-energy milling process to improve catalyst dispersion, and interaction between catalyst and the hydride may result in higher downshift of T_{dec}.

Next, we examine the effect of Ni-based catalysts on the dehydrogenation kinetics of MgH_2. The apparent activation energies, E_A being determined using the Kissinger method as previously discussed (Figure 5). Apparent E_A for the as-received MgH_2 is ~169 kJ/mol, which is in agreement with E_A obtained from the Arrhenius plot (E_A= ~168 kJ/mol) [11]. The apparent E_A for the dehydrogenation reactions of MgH_2 catalyzed by Ni_5Zr_2, $LaNi_5$, and Ni are 79, 122, and 81 kJ/mol, respectively.

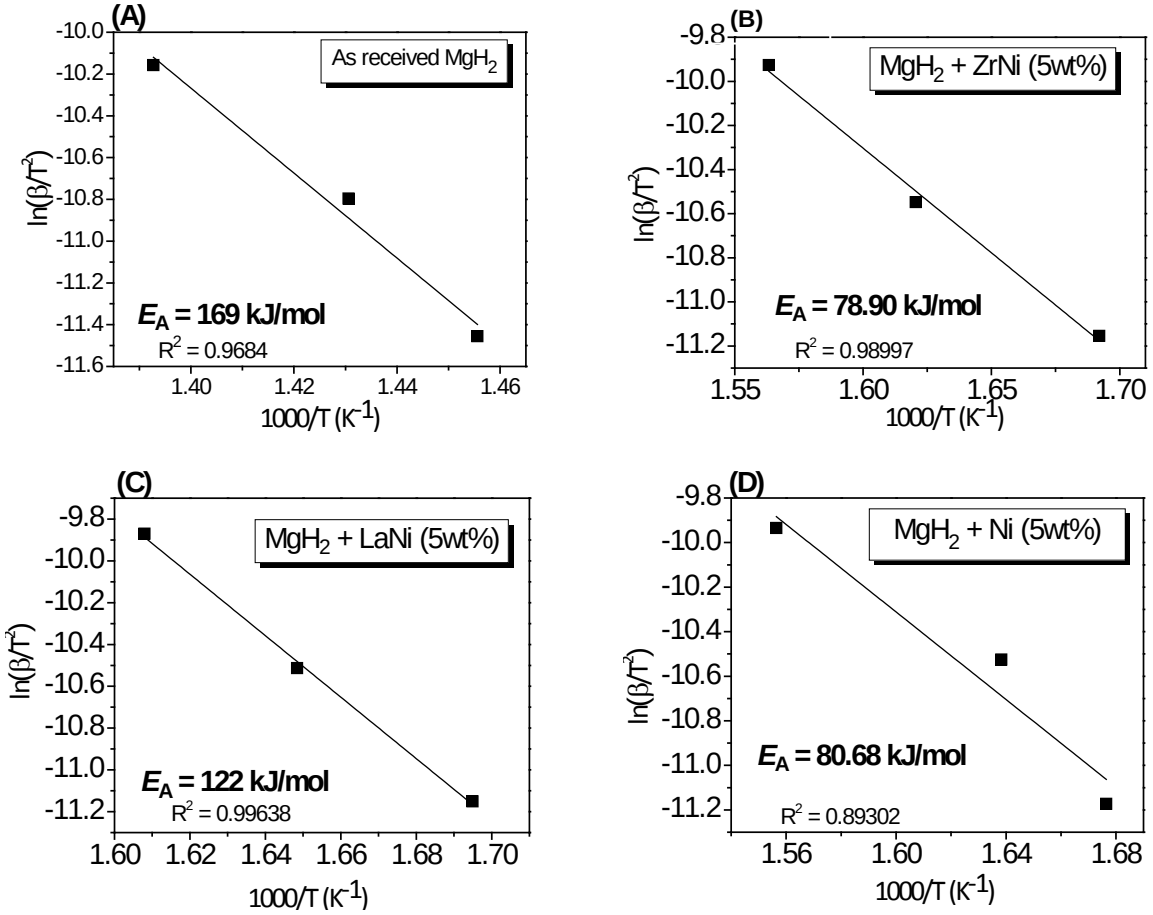

FIGURE 5 – KISSINGER PLOTS OF THE DEHYDROGENATION REACTION FOR THE (A) AS-RECEIVED MgH_2, MgH_2 MILLED WITH (B) 5 wt% Ni_5Zr_2, (C) $LaNi_5$, AND (D) Ni

From the activation energies, it is clear that modifying MgH_2 with Ni_5Zr_2 or Ni catalysts via high-energy milling improves the kinetics significantly; the E_A is reduced by half. Varin et al. [11] showed that milling MgH_2 with nano-Ni particles for 15 min and 20 h reduces the desorption temperature at atmospheric pressure to 243 and 302°C, respectively, from 418°C. The E_A of desorption of MgH_2 milled with nano-sized for 15 min and micron-sized Ni particles for 20 h are 92 and 105 kJ/mol, respectively. The E_A values obtained in our work using Ni and Ni_5Zr_2 particles are comparable to these values.

In the case of $Ca(BH_4)_2$, high-energy milling with Ni_5Zr_2, $LaNi_5$, and Ni catalysts was also performed and their impact on the H_2 T_{dec} and the dehydrogenation kinetics was studied. Table 4 gives a summary of their properties. The DSC and corresponding TGA profiles of $Ca(BH_4)_2$ modified with 2 wt% (Figure 6) and 5 wt% (Figure 7) of catalyst reveal that the only catalyst that has a positive impact on the dehydrogenation reaction is Ni_5Zr_2 (5 wt%).

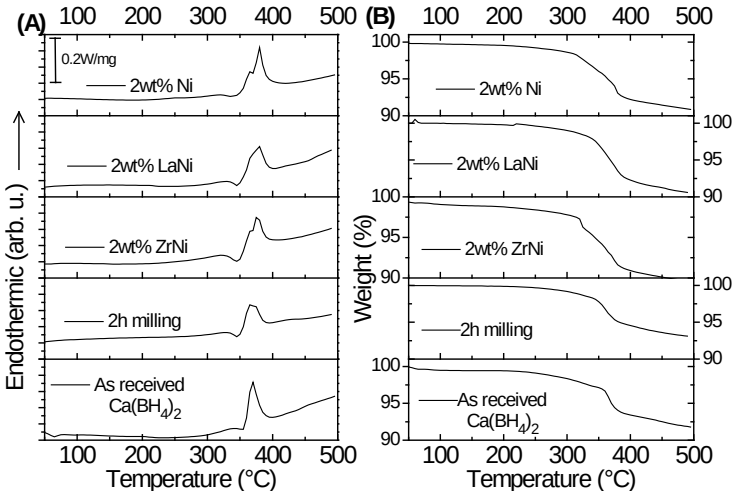

FIGURE 6 – DSC (A) AND CORRESPONDING TGA (B) PROFILES FOR THE AS-RECEIVED $Ca(BH_4)_2$, MILLED $Ca(BH_4)_2$, AND $Ca(BH_4)_2$ MILLED WITH 2 wt% CATALYSTS

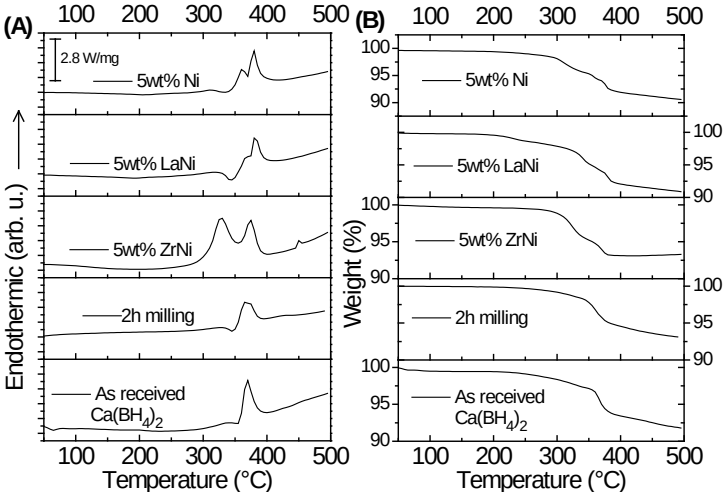

FIGURE 7 – DSC (A) AND CORRESPONDING TGA (B) PROFILES FOR THE AS-RECEIVED $Ca(BH_4)_2$, MILLED $Ca(BH_4)_2$, AND $Ca(BH_4)_2$ MILLED WITH 5 wt% CATALYSTS

The T_{dec} for the as-received $Ca(BH_4)_2$ is 370°C and T_{dec} for milled $Ca(BH_4)_2$ is 366°C while samples milled with 5 wt% of Ni_5Zr_2, $LaNi_5$ and Ni show a T_{dec} of 327, 381, and 380°C, respectively. The E_A of the dehydrogenation reaction determined via the Kissinger method for the as-received $Ca(BH_4)_2$ is 163 kJ/mol while E_A for samples doped with 5 wt% Ni_5Zr_2, $LaNi_5$, and Ni are 159, 270, and 207 kJ/mol, respectively. Clearly, the $LaNi_5$ and Ni catalysts are not providing a benefit, suggesting that the specific chemistry of the catalyst is very important in controlling E_A and T_{dec}. We are currently optimizing the milling conditions for $Ca(BH_4)_2$ while investigating the influence of other metal catalysts on the dehydrogenation properties.

TABLE 4 – PROPERTIES OF $Ca(BH_4)_2$ SAMPLES

Samples	**Catalyst amount (wt%)**	**Milling time (h)**	T_{onset} **(°C)**	T_{dec} **(°C)**
$Ca(BH_4)_2$ (Aldrich)	-	-	359	369
$Ca(BH_4)_2$	-	2	354	364
$Ca(BH_4)_2/Ni_5Zr_2$	2	2	364	377
$Ca(BH_4)_2/LaNi_5$	2	2	355	379
$Ca(BH_4)_2$/Ni	2	2	345	378
$Ca(BH_4)_2/Ni_5Zr_2$	5	2	352	374
$Ca(BH_4)_2/LaNi_5$	5	2	261	318
$Ca(BH_4)_2$/Ni	5	2	289	324

CONCLUSIONS

Using a combination of high-energy vibrating-mill technique and Ni-based catalysts, we have successfully reduced the T_{dec} of MgH_2 by ~100°C, from 414 to 318°C. MgH_2 milled for 2 h with Ni (5 wt%) and Ni_5Zr_2 (5 wt%) showed E_A of 81 and 79 kJ/mol, respectively, corresponding to ~50% decrease in E_A. These improvements were achieved after only 2 h of milling indicating the efficiency of our high-energy milling process. With the exception of Ni_5Zr_2, the Ni-based catalysts do not seem to catalyze the dehydrogenation reaction of $Ca(BH_4)_2$. Pure Zr and other catalyst chemistries will be explored in future studies. Although the improved dehydrogenation properties of the modified MgH_2 are still below the requirements for TES, our results show that high-energy vibratory ball milling combined with Ni or Ni_5Zr_2 catalyst holds promise for substantially improving the dehydrogenation kinetics and reducing T_{dec} of MgH_2.

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